IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of
Hiroyuki Fujisaki et al
Serial No. 09/777,853
Filed: February 7, 2001

Group Art Unit: 1754
Examiner:
Peter J. Lish

For: COMBUSTION CATALYST AND PROCESS FOR REMOVING ORGANIC COMPOUNDS

DECLARATION UNDER 37 C.F.R. § 1.132

Honorable Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

I, Wataru Kobayashi, of 2-9, Madokoro 4-chome, Shinnanyo-shi, Yamaguchi, 746-0012 Japan, being duly sworn, declare and state:

THAT I have been employed since April 1991 by Tosoh Corporation on the research staff of the corporation where I have been engaged in the study of development of zeolites as adsorbents and catalysts.

THAT I am a co-inventor of the invention disclosed in the above-identified U.S. patent application, and hence I am fully familiar therewith.

THAT, to demonstrate that the pore size distribution characteristics of alumina of the first catalyst is important for combustion of hydrocarbons at an enhanced conversion at a relatively low combustion temperature, the following comparative xperiments were carried out.

COMPARATIVE EXPERIMENTS

TRANSLATION OF "EXAMPLE 1" OF JAPANESE APPLICATION NO. 2000-34331

[0034]

<u>Examples</u>

Example 1 (Preparation of Catalyst 1)

An alumina material (commercially available from Sumitomo Chem. Co., Ltd. under the trademark of "TA-1301") in an amount of 20 g was added into 180 ml of a 28.5 mM aqueous solution of dinitro-diammine platinum. The resulting mixture was stirred at 30°C for 2 hours and then separated into solid-liquid phases. The solid phase was washed with pure water and dried at 110°C for 20 hours to give a platinum-loaded alumina.

By ICP emission spectroscopy, a platinum content of 4.3% by weight was found, but no rare earth elements were detected. By nitrogen adsorption method, it was determined that the alumina had such a pore distribution that, where "a" represented a pore radius in Å at the maximum of the pore size distribution curve, the accumulated pore volume of pores having radii in the range of "a" ± 25Å was 90% of the total volume of all the pores. The platinum-loaded alumina was used as a first catalyst.

[0035]

A beta type zeolite having a SiO_2/Al_2O_3 molar ratio of 25.7 (commercially available from Tosoh Corporation under the trademark "HSZ-930-HOA") in an amount of 50 g was introduced into 450 ml of a 0.69 M aqueous calcium chloride solution. The resulting mixture was stirred at 60°C for 20 hours to effect ion-exchange. The slurry was separated into solid and liquid phases, and the resulting zeolite cake was added into 450 ml of a 0.69 M aqueous calcium chloride solution to effect again ion-exchange with stirring at 60°C for 20 hours. After solid-liquid separation, the solid cake was washed repeatedly with pure water until no chloride ion was detected in the filtrate. Then the solid was dried at 110°C for 20 hours to give a calcium-form beta.

[0036]

A 8 g portion of the calcium-form beta and a 2 g portion of the above-obtained platinum loaded-alumina were combined together and mixed thoroughly to give a second catalyst.

[0037]

Each of the first catalyst and the second catalyst was pelletized, crushed and graded into 12 to 20 mesh. A 1 ml (0.75 g) sample of particles in such a size range of the first catalyst and a 1 ml (0.5 g) sample of particles in such a size range of the second catalyst were packed in an upstream part and a downstream part, respectively, of an atmospheric-pressure fixed bed reactor to give "Catalyst 1".

(1) <u>Preparation of Catalysts</u>

Example 1

An alumina material (commercially available from Sumitomo Chem. Co., Ltd. under the trademark of "TA-1301") in an amount of 20 g was added into 180 ml of a 28.5 mM aqueous solution of dinitro-diammine platinum. The resulting mixture was stirred at 30°C for 2 hours and then separated into solid-liquid phases. The solid phase was washed with pure water and dried at 110°C for 20 hours to give a platinum-loaded alumina.

By ICP emission spectroscopy, a platinum content of 4.3% by weight was found, but no rare earth elements were detected. By nitrogen adsorption method, it was determined that the alumina had such a pore distribution that, where "a" represented a pore radius in Å at the maximum of the pore size distribution curve, the accumulated pore volume of pores having radii in the range of "a" ± 25Å was 90% of the total volume of all the pores. The platinum-loaded alumina was used as a first catalyst.

A beta type zeolite having a SiO_2/Al_2O_3 molar ratio of 25.7 (commercially available from Tosoh Corporation under the trademark "HSZ-930-HOA") in an amount of 50 g was introduced into 450 ml of a 0.69 M aqueous calcium chloride solution. The resulting mixture was stirred at 60°C for 20 hours to effect ion-exchange. The slurry was separated into solid and liquid phases, and the resulting zeolite cake was added into 450 ml of a 0.69 M aqueous calcium chloride solution to effect again ion-exchange with stirring at 60°C for 20 hours. After solid-liquid separation, the solid cake was washed repeatedly with pure water until no chloride ion was detected in the filtrate. Then the solid was dried at 110°C for 20 hours to give a calcium-form beta.

A 8 g portion of the calcium-form beta and a 2 g portion of the above-obtained platinum loaded-alumina were combined together and mixed thoroughly to give a second catalyst.

Each of the first catalyst and the second catalyst was pelletized, crushed and graded into 12 to 20 mesh. A 1 ml (0.75 g) sample of particles in such a size range of the first catalyst

and a 1 ml (0.5 g) sample of particles in such a size range of the second catalyst were packed in an upstream part and a downstream part, respectively, of an atmospheric-pressure fixed bed reactor to give "Catalyst 1".

Example 2

By the same procedures as described in Example 1, a platinum-loaded alumina was prepared wherein 180 ml of a 5.70 mM aqueous solution of dinitro-diammine platinum was used with all other conditions remaining the same. By ICP emission spectroscopy of the resultant platinum-loaded alumina, a platinum content of 1.0% by weight was found, but no rare earth elements were detected. By nitrogen adsorption method, it was determined that the alumina had such a pore distribution that the accumulated pore volume of pores having radii in the range of "a" ± 25Å was 90% of the total volume of all the pores. The platinum-loaded alumina was used as a first catalyst.

A portion of the second catalyst as prepared in Example 1 was used as a second catalyst.

Each of the first catalyst and the second catalyst was pelletized, crushed and graded into 12 to 20 mesh. A 1 ml (0.75 g) sample of particles in such a size range of the first catalyst and a 1 ml (0.5 g) sample of particles in such a size range of the second catalyst were packed in an upstream part and a downstream part, respectively, of an atmospheric-pressure fixed bed reactor to give "Catalyst 2".

Comparative Example 1

A portion of the platinum-loaded alumina as prepared in Example 1 was pelletized, crushed and graded into 12 to 20 mesh. A 2 ml sample of particles in such a size range was packed in an atmospheric-pressure fixed bed reactor to give "Comparative Catalyst 1".

Comparative Example 2

A 8 g portion of the calcium-form beta as prepar d in Example 1 and a 2 g portion of the platinum-loaded alumina as

prepared in Example 1 were combined and mixed together. The mixture was pelletized, crushed and graded into 12 to 20 mesh. A 2 ml sample of particles in such a size range was packed in an atmospheric-pressure fixed bed reactor to give "Comparative Catalyst 2".

Comparative Example 3

A 1 ml (0.5 g) portion of the second catalyst as prepared in Example 1 and a 1 ml (0.75 g) portion of the first catalyst as prepared in Example 1 were packed in an upstream part and a downstream part, respectively, of an atmospheric-pressure fixed bed reactor to give "Comparative Catalyst 3".

Comparative Example 4

By the same procedures as described in Example 1, a platinum-loaded alumina was prepared wherein an alumina material (commercially available from Catalysts and Chemicals Industries Co., Ltd. under the trademark of "ACP-1") was used instead of "TA-1301" commercially available from Sumitomo Chem. Co., Ltd. with all other conditions remaining the same.

By ICP emission spectroscopy of the resultant platinum-loaded alumina, a platinum content of 4.3% by weight was found, but no rare earth elements were detected. By nitrogen adsorption method, it was determined that the alumina had such a pore distribution that the accumulated pore volume of pores having radii in the range of "a" ± 25Å was 49% of the total volume of all the pores. The platinum-loaded alumina was used as a first catalyst.

A 8 g portion of calcium-form beta obtained in Example 1 and a 2 g of the above-obtained platinum loaded-alumina were combined together and mixed thoroughly to give a second catalyst.

Each of the first catalyst and the second catalyst was pelletized, crushed and graded into 12 to 20 mesh. A 1 ml (0.75 g) sample of particles in such a size range of th first catalyst and a 1 ml (0.5 g) sample of particles in such a size range of the second catalyst were packed in an upstream part and a downstream part, r spectively, of an atmospheric-pressure fixed

bed reactor to give "Comparative Catalyst 4".

Comparative Example 5

A portion of the first catalyst as prepared in Comparative Example 4 was used as a first catalyst. A portion of the second catalyst as prepared in Example 1 was used as a second catalyst.

Each of the first catalyst and the second catalyst was pelletized, crushed and graded into 12 to 20 mesh. A 1 ml (0.75 g) sample of particles in such a size range of the first catalyst and a 1 ml (0.5 g) sample of particles in such a size range of the second catalyst were packed in an upstream part and a downstream part, respectively, of an atmospheric-pressure fixed bed reactor to give "Comparative Catalyst 5".

(2) Evaluation of Catalyst Performance

Each of Catalysts 1 and 2 prepared in Examples 1 and 2, and Comparative Catalysts 1 through 5 prepared in Comparative Examples 1 through 5 was pretreated by passing therethrough an air stream at 500°C for 1 hour. After the pretreatment, the fixed bed was cooled down to a temperature of 100°C and a gas having a composition as shown in Table 1 was passed through the fixed bed at a flow rate of 360 ml/min., while raising the temperature at a heating rate of 10°C per minute.

Table 1

Gas Composition (by volume)	
1,2-dichloroethane	2,000 ppm
Ethylene	6,000 ppm
O_2	11.1%
H_2O	0.3%
N_2	Balance

Temperatures at which conversions of the total hydrocarbons in the bed gas stream reached 95% and 99% were measured. Table 2 shows temperatures at which 95% and 99% of the total hydrocarbons were obs rv d.

Table 2

Conversion Attained at Temperatures (℃)

	Composition of catalyst		Conversion attained at temp. (℃)	
	First catalyst	Second catalyst	95% Conversion	99% Conversion
Catalyst 1	Pt 4.3%/Al*1	Ca-β-zeolite + Pt 4.3%/Al*1	196	235
Catalyst 2	Pt 1.0%/Al*1	Same as above	235	272
Comparative Catalyst 1	Pt 4.3%/Al*1	-	318	395
Comparative Catalyst 2	-	Ca-β-zeolite + Pt 4.3%/Al*1	300	314
Comparative Catalyst 3	Ca-β-zeolite + Pt 4.3%/Al*1	Pt 4.3%/Al*1	471	482
Comparative Catalyst 4	Pt 4.3%/Al*2	Ca-β-zeolite + Pt 4.3%/Al*2	280	350
Comparative Catalyst 5	Pt 4.3%/Al*2	Ca-β-zeolite + Pt 4.3%/Al*2	275	335

Note Al*1: accumulated pore volume of pores having radii of (a ± 25) angstrom is 90%
Al*2: accumulated pore volume of pores having radii of (a ± 25) angstrom is 49%

Received at: 10:10AM, 6/12/2003
2003年 6月12日 22時45分 UCHIDA&ASSOCIATES NO. 6560 P. 13

As seen from Table 2, especially from comparison of Catalyst 1 (Present Invention) with Comparative Catalyst 4 and Comparative Catalyst 5, the accumulated pore volume of pores having radii in the range of a ± 25 angstrom of alumina in the first catalyst (said accumulated pore volume is hereinafter referred to merely as "accumulated pore volume") is important for attaining a high conversion of hydrocarbons at a relatively low temperature.

That is, in the case when alumina having 4.3% by weight of platinum loaded thereon had an accumulated pore volume of 90% (Catalyst 1), 95% conversion and 99% conversion were obtained at 196°C and 235°C, respectively.

In contrast, in the case when alumina having 4.3% by weight of platinum loaded thereon had an accumulated pore volume of 49% (Comparative Catalyst 4 or Comparative Catalyst 5), 95% conversion and 99% conversion were obtained at 280°C or 275°C, and 350°C or 335°C, respectively.

I, the undersigned declarant, declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and; further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001, of Title 18, of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

This tenth day of June, 2003

Wataru Kobayashi

Wataru Kobayashi

2003年 6月12日 22時46分 UCHIDA&ASSOCIATES NO. 6560 P. 14
Received at: 10:10AM, 6/12/2003